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Enhanced performance based on a hybrid cathode backing layer using a biomass derived activated carbon framework for methanol fuel cells

Prabhuraj Balakrishnan,a I. Isil Gurten Inal,b Emily Cooksey,a Anthony Banford,a Zeki Aktasb and Stuart M. Holmes*a

Highlights:
1. Activated carbon prepared from factory waste-tea possessed 75.69 % of mesopores and 24.31 % of micropores.
2. This activated carbon used as cathode microporous layer, improved gas permeability and water removal characteristics owing to its pore size distribution and particle size characteristics.
3. The MEA incorporated with activated carbon improved fuel cell performance to 33% and enhanced stability, when tested in general operating conditions.

Graphical Abstract

**Graphical abstract:** Illustration of enhanced power performance attributed to the usage of activated carbon.
Abstract

Direct methanol fuel cells (DMFCs) suffer from performance reduction due to mass transport losses incurred at high current regions. In this work, we report the use of activated carbon (AC), prepared from factory waste-tea, as cathode microporous layer in the membrane electrode assembly (MEA) of a DMFC, alleviating this mass transport effect. This biomass based AC framework, when tested under fuel cell operating conditions provided 0.25 V @ 300 mA cm\(^{-2}\), enhancing cell performance by 33 % over standard electrodes at 70 °C. During uninterrupted durability testing, this electrode displayed exceptional stability in mass transport dominated region, with loss of 15 mV day\(^{-1}\), compared to 25 mV day\(^{-1}\) loss for the standard. Sample and electrode characterization measurements reveal that pore size distribution/particle size characteristics coupled with hydrophobic nature of the synthesized activated carbon, contributed to the performance improvement.

Keywords: Direct methanol fuel cells; Microporous layer; Carbon; Activated carbon; Improved power density.

1. Introduction

In the recent years, fuel cells have emerged as alternatives to conventional energy technologies, driven by greenhouse gas emission from fossil fuels [1, 2, 3]. Fuel cells have benefits in many areas namely reduced environmental impact, zero noise, and simple operational mechanisms [1, 3]. Among several fuel cell types, direct methanol fuel cells (DMFCs) are favoured due to their flexibility in the usage of liquid fuel rather than hydrogen which can be difficult to transport and store, low temperature operation and suitability for use in portable applications [3, 4].

However, DMFC commercialisation is greatly hindered by several limitations including mass transport loss [2, 4]. Mass transport loss can be defined as increased resistance in accessing catalyst sites by the reactant molecules caused by the formation of water molecules on the cathode electrode which is more significant in high current regions, when large quantities of water are produced but the ‘turn over’ of the catalyst is high [1, 4]. This also results in poor oxidant utilization efficiency [1, 3, 4].

This mass transport limitation mainly occurs in the backing layer of the membrane electrode assembly (MEA) [3, 4]. The MEA can be defined as the heart of fuel cell in which the proton exchange membrane is sandwiched between two electrodes, where the oxidation and reduction reactions take place [4, 5]. The backing layer comprises of a microporous layer (MPL) and a gas diffusion layer (GDL). The MPL plays a major role in many factors including, effective transfer of reactants from the GDL to the catalyst layer, maintaining effective electrical contact between GDL and MPL and effective water removal from the cathode electrode [4, 5, 6].

Several articles in the literature have reduced this mass transport effect by controlling external or internal factors [7-10]. In terms of external factors, efforts like increasing air flow rate to force the condensing water molecules out [7], increasing the
compression force applied on the MEA so that the distance between the reactant and catalyst sites decreases [8] were followed. These strategies often result in adding more complexity and economic cost to fuel cell [7, 8].

Internal control factors, involve incorporating the MEA with new materials [9-14]. The approaches are further classified into using carbon precursors with optimized pore structure and varying the degree of hydrophobic/hydrophilic nature of electrode materials. Using optimized pore structure will help to create more pathways for reactant molecules to access the catalyst sites. Several authors have worked on different carbon precursor materials and shown that the presence of an optimized pore structure will help to create more pathways in addition to effective removal of product molecules, for improved performance [9, 10, 11].

A further approach is increasing hydrophobicity, which plays a role in the effective removal of water molecules from the electrode by creating a pathway for reactants. This is facilitated by using poly tetrafluoro ethylene (Teflon) [12], poly vinylidene fluoride [13] or perfluropolyether derivative [14] in the MPL of the MEA. However these are typically electrical insulators, which are detrimental to fuel cell operation as the decrease in electrical conductivity of MPL affects the reaction kinetics and increases ohmic loss. So a balance is made between the amounts of these polymers and carbon precursor, such that the conductivity of the electrode is not significantly affected. Ketjen Black (KB) is widely used as carbon precursor in the microporous layer of a DMFC because of its excellent pore structure and electrical conductivity properties, when compared to other commonly used carbon materials, such as Acetylene Black, Black Pearl, Vulcan XC-72, Furnace black [15]. Despite this, it still suffers from poor performance at high current density. Hence there is a need for a better material with a good pore structure suitable for use in cathode electrode of DMFCs.

Activated carbons (AC) are a class of materials, prepared from a wide variety of cheap/abundant precursor sources such as nutshells, peat, wood, coal, lignite etc [16,17]. These AC materials are reported to have wide range of pore characteristics and surface areas (depending on the preparation conditions and source material), hence their current usage in energy applications such as supercapacitors, ultracapacitors, electrical double layer capacitors, and hydrogen storage [16, 17, 18]. The pore characteristics are an attractive feature for use as electrodes in fuel cells, where optimized pore structure is desirable, to facilitate improved gas transfer with the catalyst sites with simultaneous removal of water from the electrode and conductivity of electrons. In this work, we report the usage of an activated carbon prepared from waste tea, at the cathode electrode in a DMFC. In our previous work, we have used this activated carbon in supercapacitors and obtained considerable improvement in performance [19]. Several articles have been reported to have used AC, in the catalyst layer of fuel cells [20, 21], however we report for the first time, the use of AC in the microporous layer of a DMFC system.

In addition, the methodology used for the production of conventionally used carbon precursors involves treating hydrocarbons in a furnace at high temperature and pressure. This leads to the release of harmful environmental pollutants SOx and NOx into atmosphere [16]. The activated carbon prepared from biomass based waste-tea, reported in this work is ready available and abundant [16, 17]. The simplified
preparation methodology adopted and precursor used, tend to minimize the harmful pollutants.

2. Materials and methods
2.1. Preparation of activated carbon
The activated carbon was produced from waste-tea by a microwave pretreatment-integrated method using phosphoric acid ($\text{H}_3\text{PO}_4$) as an activation agent as reported in previous articles (Inal et.al [19], Yagmur et.al [22] as follows (given in the Fig. S1): Waste-tea collected from a tea factory in the Eastern Black Sea region of Turkey, is first crushed and samples under 500 µm were selected after sieving. After treatment with 85 wt% phosphoric acid solution (Merk), samples underwent microwave pre-treatment for 30 seconds and carbonised at 450 °C for 60 minutes in a nitrogen atmosphere. Then the samples are washed with de-ionised water and dried at 110 °C overnight.

2.2. Characterisation of the activated carbon
The characterisation of the carbon samples was carried out by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Particle size distribution, Nitrogen adsorption-desorption isotherm and pore size distribution analyses techniques. SEM and EDS analysis used an FEI Quanta 200 microscope, after coating samples with thin gold layer. Particle size distributions were obtained using a Malvern Mastersizer 2000, Hydro 2000 MU by laser diffraction. Nitrogen adsorption-desorption isotherms and pore size distribution analyses techniques were performed using Quantachrome NOVA 2200 gas adsorption equipment. The total surface area were measured according to Brunauer-Emmett-Teller (BET) method, using nitrogen-adsorption isotherm data (below $P/P_0=0.35$). The micropore volume was determined by interpolation at 2 nm using non-density local functional theory and is subtracted from total pore volume to obtain mesopore volume.

2.3. Membrane electrode assembly fabrication
The MEA is fabricated as shown in Fig. S2 [23] as follows: First, the MPL is prepared by spraying carbon ink onto Toray carbon paper TGP-090 (280 µm, Fuel cell store) of size 4.5 cm x 4.5 cm. The carbon ink contains Ketjen Black (EC- 600 JD, Akzo Nobel) with PTFE (Poly tetra fluro ethylene, 20 wt % solution from Sigma Aldrich) in 10 wt% dissolved in iso-propanol (99 % purity, Sigma Aldrich). This MPL along with GDL is sintered at 300° C for 3 hours in an oven. Then catalyst ink is sprayed over the MPL up to a Pt loading of 1 mg cm$^{-2}$ for both anode and cathode. Catalyst ink contains catalyst (60 wt % Pt on Vulcan XC-72 for cathode and 60 w t% Pt:Ru on anode) with 15 wt % Nafion ionomer (20 wt % solution from Sigma Aldrich) dissolved in acetone (ultrasonically agitated and with vigorous mechanical stirring to form a homogeneous ink). Then 1 mg cm$^{-2}$ of Nafion is sprayed over catalyst layer to enhance interfacial contact between the catalyst layer and Nafion membrane. Nafion® 117 (183 µm thickness, Sigma Aldrich) membrane is pre-treated by heating in de-ionised water, 10 wt % hydrogen peroxide (98% purity, Alfa Aesar) and 1 M sulphuric acid (98% purity, Sigma Aldrich) solutions at 80 °C for an hour approximately. The MEA is fabricated by placing a Nafion membrane in between the anode and cathode and fixing in fuel cell test system.
The cell was activated at 70°C by air-starvation mode [24] by passing 1 M Methanol (50 mL min⁻¹) and 1 L min⁻¹ (2 bar) of air, until the optimum performance was achieved, as shown by a stable polarization curve.

In this work, to prepare activated carbon (AC) cathode MPL, AC is mixed with Ketjen Black (KB) at different weight percentages with ultra-sonication for 3 hours, 5 wt %, 10 wt %, 15 wt %, 20 wt %, 25 wt %, 50 wt %, 75 wt % and 100 wt %. All other materials used for the MEA preparation, remained the same.

2.4. Electrode characterization-measurements and methods

2.4.1. Wettability-contact angle measurements

In order to determine the degree of hydrophobicity of the carbons, a 5 µL drop of water was placed on a small sample of each electrode and after 3 minutes the contact angle was measured between the droplet and the electrode surface, using a Gonio Star 150 [25].

2.4.2. Porosity (hydrophobic and hydrophilic)

This is obtained by immersing the electrode in n-decane solvent, which fills the pores in the electrode followed by weighing the electrodes. The porosity is calculated from weight difference of electrodes before and after immersion in the solvent and then divided by the density of n-decane [26, 27]. Hydrophilic porosity is obtained by placing the sample horizontally in a home-made apparatus, as given in the Fig. S3(a-c). Water is vaporized by placing the apparatus in an oven. On vaporization, the sample weight is increased as a result of capillary condensation in the pores. Weight of the sample is measured before and after, to calculate hydrophilic porosity. Hydrophobic porosity is calculated by subtracting hydrophilic porosity from total porosity.

2.4.3. Gas permeability

Gas permeability of the electrodes was obtained using standard volume method [28] by placing electrodes in a test cell as shown in Fig. S4 and calculated according to the following equation.

\[
\text{Permeability} = \frac{N \times T}{p_1 - p_2}
\]

Where, permeability given in barrer; N is steady state penetrant flux (cm³ cm⁻² s⁻¹); p₁ and p₂ are feed and permeate side pressure (cm of Hg); T is electrode thickness (cm). Nitrogen gas is used for these electrode permeability measurements, to give results close to the air permeability, as used in fuel cell polarization measurements. (Oxygen and nitrogen have the same Van der Waals radius of 155 pm).

2.4.4. Through-plane and in-plane electrical conductivity of microporous layer

Through-plane conductivity of the MPL is obtained by placing the material between two platinum sheets of size 4.0 x 0.9 cm and then running the impedance spectroscopy in the frequency range from 20 kHz to 0.01 Hz at amplitude of 10 mV and calculated according to the formula below [29, 30].
Through plane conductivity = \frac{T}{R \times A}

Where, Through-plane conductivity is expressed in S cm\(^{-1}\); T is Electrode thickness (cm); R is Resistance obtained from x-axis intercept of impedance plot (\(\Omega\)); A is Electrode area of platinum (cm\(^2\)).

In-plane conductivity of the MPL (carbon ink coated on GDL) is obtained by four platinum sheets of size 4.0 x 0.9 cm at a distance of 0.5 cm on the MPL (facing the layer as given in Fig. S5) and then running the impedance spectroscopy under the same conditions [29, 30].

\[ \text{In-plane conductivity} = \frac{D}{R \times W \times T} \]

Where, In-plane conductivity of electrode is given in S cm\(^{-1}\); D- Distance between platinum electrodes (cm); R is Resistance obtained from x-axis intercept of impedance plot (\(\Omega\)); W is Width of platinum electrode (cm); T is Electrode thickness (cm).

2.5. Polarization curves were obtained by a potentiostatic method (linear sweep voltammetry) by AUTOLAB PGSTAT 30 equipment from Open Circuit Voltage (OCV) to 0 V at a scan rate of 0.25 mV per second [23].

2.6. Membrane electrode assembly reaction resistance is obtained by impedance spectroscopy (potentiostatic) in a working fuel cell in the frequency range from 20 kHz to 0.01 Hz at amplitude of 10 mV as described in the procedure [31, 32]. The MEA resistance in the activation region is measured at potentials corresponding to activation region (at 0.6 V), whereas resistance in ohmic resistance is measured at potentials in ohmic region (at 0.3 V), and the mass transport resistance is measured at potentials in high current density regions (0.1 V).
3. Results and discussion

3.1. Characterization of the activated carbon

Table 1 gives the elemental composition analysis (EDS) of synthesized activated carbon sample. The oxygen and nitrogen functional groups arise from phosphoric acid treatment and carbonisation steps, during the preparation process of the sample from waste-tea, as explained in Fig. S1 [18, 22]. Nitrogen adsorption-desorption isotherm (Fig. 1a) determined pore volume to about 1.142 cm$^3$ g$^{-1}$ and BET surface area of 1327 m$^2$ g$^{-1}$ and tabulated in Table 2. Pore size distribution measurements (from Fig. 1b) reveal that the sample has 75.69 % of mesopores and 24.31 % of micro pores. This is of significant interest, as studies have stressed the importance of materials containing sufficient micro/meso pores essential to provide gas transport in addition to the water removal across the cathode electrode in DMFCs [6, 7, 33, 34].

During their operation, water transport tends to occur in the mesopores, whereas gas transport occurs in both meso and micropore channels in the MPL [6, 7]. Hiramitsu et.al [33] introduced a microporous layer to the GDL, and showed increased water removal from the electrode giving improved performance. Wang et.al [34] reported a composite microporous layer comprising of Acetylene Black and Black Pearl for improved performance. In their work, they have shown that 10 wt% Black Pearl-Acetylene Black electrode composition, exhibited improved water removal with gas permeability characteristics by utilizing the hydrophilic porosity nature of Black pearl and higher pore volume of Acetylene Black, leading to performance improvement.

Ketjen Black (KB) has 95% of mesopores and 5% of micro pores (from pore size distribution and nitrogen adsorption desorption isotherm measurements Table 2). Since, mesopores are completely filled with water during high current density operation, micropores are the only available route for the air to reach catalyst sites [7,9,10]. As a result, Ketjen Black suffers from mass transport losses, due to the insufficient micropores available for gas transport, the activated carbon sample has higher percentages of micropores. Hence this AC is expected to facilitate water removal in the cathode.

3.2. Different activated carbon wt % electrode characteristics and fuel cell performance

Fig. 2 shows the SEM images of electrodes coated with KB and different weight percentages of AC. It can be seen that the average crack size increased for 15 wt% AC electrode (Fig. 2b), compared to standard (Fig. 2a). On further increasing the AC wt %, the cracks disappeared and show agglomerated surface (Fig. 2c-2f).

The particle size results (from Fig. 3 and Table S1) show that the synthesised activated carbon sample is coarser than Ketjen black at the particle size above 10 μm. The
morphology was discussed in greater detail in our previous study [19]. The distribution
curves of the samples also clearly show that the particles of the activated carbon are
more heterogeneous than the KB. The 0% AC samples show good performance and
are cracked and these cracks are known to promote easier water transport across the
electrode [35, 36, 37] as the concentration of AC increases, the effect of the different
chemical structure, different particle size and the morphology appears to enhance
these cracks. However, once the concentration of AC becomes greater than 15% the
homogeneity of the carbon increases and the crack formation is reduced until (above
25 wt%) when a smooth surface with poor water transport is produced. Poor water
transport leads to flooding of the catalyst layer and hence reduced performance of the
fuel cell.

The contact angle measurements from Table 3, show that the MPL coated with AC
exhibited higher contact angle values than Ketjen Black of 106° ± 1. This shows that
the surface is more hydrophobic as expected from the literature quoted hydrophobic
nature of activated carbon samples [16, 17, 18] and the results of the XPS data which
were reported in our previous work [19] in synthesising this material which showed a
mixture of oxygen containing species on the surface. The AC made from waste tea
was shown to have carbonyl, carboxylic and hydroxyl groups on the surface. This is of
significant advantage, when used as electrodes so as to eliminate flooding effect in
fuel cells. Yan et. al [25] used fluorinated carbon nanotubes (CNTs) with higher contact
angle than conventional material and reported an improved water removal rate than
the conventional electrode.

Porosity measurements of different electrodes (Table 3) were carried out as explained
in the experimental procedure. The hydrophobicity of AC electrodes increased with
the AC content, higher than that of KB electrode.

Fuel cell experiments were carried out at 30°C to 70°C temperature range, with 1 M
methanol and air (1 litre per minute) as general operating conditions. On increasing
the AC wt %, the peak power density improved from 55 mW cm⁻² for the standard to
58 mW cm⁻² for 5 wt % AC and then to 65 mW cm⁻² for 10 wt % AC. Among these, AC
15 wt% composition electrode exhibited a significant increase in power density of up
to 72 ± 3 mW cm⁻², around 33% improvement (Fig. 4a and Fig. 4b). It can be seen
from the current-voltage profile (Fig. 4a) that significant changes occur in the high
current density region i.e. after 200 mA cm⁻².

On further increasing the AC content above 15 wt%, the performance drastically
dropped from 55 mW cm⁻² (standard) to 40 mW cm⁻² for 50 wt % AC, then to 25 mW
cm⁻² for 100 wt % AC (Fig. 4c and Fig. 4d).

In general, fuel cell polarization curve exhibit three regions namely activation loss,
ohmic loss and mass transport loss [3, 4] during their operation as given in Fig. 4e.
The activation region is attributed to the factors such as electrical conductivity, catalytic
activity corresponding to the type and amount of catalyst loading, type of electrode
[31]. Ohmic region corresponds to the protonic conductivity of the electrolyte i.e. the
membrane [31, 32]. Mass-transport region is attributed to factors such as water
removal, improved permeability corresponding to porous structure and hydrophobic
nature of electrode [32]. Hence these negligible changes in activation and ohmic
region, with major improvement in cell voltage observed in high current density regions, (from current density plots) implies that these AC electrodes has played a role in mass-transport region.

On studying the 15 wt% AC electrode, the Tafel plot from Fig. 5, shows no additional catalytic activity as given by similar values of slope for two electrodes. The In-plane and through-plane electrical conductivity measurement values (from Table S2), are lower for 15 wt% AC electrode (1.75 S cm\(^{-1}\) through-plane and 140 S cm\(^{-1}\) in-plane) than KB (1.85 S cm\(^{-1}\) through-plane and 149 S cm\(^{-1}\) in-plane) showing that AC electrode has not played a role in improving electron transfer rate. Hence confirming that this electrode has not played a role in activation region (catalytic effect), which is evident from the very slight decrease in open circuit voltage (OCV) from 0.625 V for the standard to 0.615 V for 15 wt % AC (inset of Fig. 4a). To further confirm the catalytic activity of AC electrode, this AC is tested in anode microporous layer Fig. S7a. The similar values of methanol oxidation current of 200 mA cm\(^{-2}\) (from Fig. S7b) and methanol oxidation onset potential of 0.7 V for the two electrodes observed, confirm their non-activity towards catalysis.

The gas permeability of 15 wt % AC electrode is 52 Barrer, lower than KB (60 Barrer), caused by the lower values of pore volume of 1.1 cm\(^3\) g\(^{-1}\) for AC (pore size distribution results from Table 2). It should also be noted that gas permeability were carried out as ex-situ measurements. This implies that, in actual fuel cell operation, optimized gas transfer rate together with improved water removal, has led to increased limiting current density from 350 mA cm\(^{-2}\) (standard) to 500 mA cm\(^{-2}\) (15 wt% AC). This improvement is exhibited throughout the entire temperature of operation of fuel cells from 30 °C to 70 °C, with linear improvement in peak power density obtained as given in Fig. 6.

All these polarization curves at all temperatures exhibited a similar trend i.e. changes in mass transport region, showing improvement in limiting current density and no changes in activation region, thereby showing the role of AC in mass transport effect (from Fig. S8). This improvement in mass transport is caused by the enhanced water removal rate of the electrode, by the higher crack size of this 15 wt % AC electrode (from Fig. 2b) and hydrophobic nature of electrodes (from contact angle and electrode porosity measurements from Fig. S6). Cha 2004 [35] in his work explained that the improved crack size, increases the capillary pressure within the electrodes, thereby facilitating in increased water removal rate and this behaviour is exhibited in this electrode.

MEA reaction resistance values were obtained using impedance spectroscopy [31, 32] and Fig. 7a gives the information that can be obtained from a typical impedance plot during actual fuel cell operation. The impedance plot obtained in activation (0.6 V) and ohmic regions for two electrodes (0.3 V for standard and 15 wt% AC), shows no significant difference (Fig. 7b and Fig. 7c). The higher values of resistance in activation region are attributed to the lower electrical conductivity of 15 wt% AC electrode, thereby confirming no role of 15 wt % AC in activation region, as explained before from fuel cell current density plot.
In the mass-transport region (0.1 V) impedance plot of the two electrodes (Fig. 7d), the reaction resistance has undergone a major change reducing from 2.8 $\Omega$ cm$^2$ to 1.5 $\Omega$ cm$^2$, about 60 $\%$ change in values of resistance comparable to 10 $\%$ and 0.1 $\%$ changes change in other regions (Fig. 7e). These show the role of 15 wt% AC electrode in mass transport region confirming the previous electrode characterization and fuel cell polarization results.

Durability testing helps in the evaluation of suitability of electrode materials for commercial application [38, 39]. From Fig. 8a, it is evident that the 15 wt % AC electrode, shows similar stability behaviour as the standard when tested in the lower current density region of 100 mA cm$^{-2}$. Since changes in current-voltage profile were obtained in mass transport region, testing is required at higher loads. At these values of higher current densities, formation of water molecules is rapid (leading to flooding effect), so voltage loss is quite high, so testing in this region would help better to evaluate the long term operational stability of activated carbon employed in cathode electrode [7, 8, 38].

Testing at 325 mA cm$^{-2}$ (for the standard and 15 wt % AC), as shown in the Fig. 8b, shows enhanced stability of 15 wt % AC electrode with loss of 15 mV day$^{-1}$, compared to 25 mV day$^{-1}$ loss, for the standard. Moreover, this AC electrode showed 0.180 V at 25 hours, whereas for the standard, this has dropped to 0 V, where the degradation is reversible for both standard and 15 wt% AC, using air starvation mode (cell performance recovery method) conditioning of the MEA, which led to complete recovery of cell voltage [24].

Therefore the 15 wt % electrode displayed exceptional behaviour during short term and long term tests. Whereas other electrodes, showed poor performance on increasing the AC wt% content, this is attributed to the lower electrical conductivity of AC (0.79 S cm$^{-1}$ through-plane and 88 S cm$^{-1}$ in-plane), over conventional KB (1.85 S cm$^{-1}$ through-plane and 149 S cm$^{-1}$ in-plane from Table S2). This higher value of resistance, arise from presence of oxygen functional groups on the AC substrate as discussed in elemental composition results of AC. This impact of electrical conductivity is evident from the lower values of OCV than the standard, from the inset of current density plot from Fig. 4c. Also the agglomerated surfaces of the electrodes containing AC content 25 wt % and higher, (Fig. 2c-2f) caused poor electrical contact between GDL and catalyst layer, thereby contributing to degraded performance.

In case of the electrode containing 15 wt% AC, the lower values of electrical conductivity (6 $\%$ decrease) has not prevented the electrode from decreasing the mass transport limitations. However in higher AC wt % electrodes, the electrical conductivity became a dominant factor and declined the performance. As given by Fig. 9, the AC has played a role in mass transport region by showing improved water removal, owing to its pore characteristics; however on increasing the wt % above 15, the poor electrical conductivity has led to decline in performance.

4. Conclusion

Results show that this activated carbon, when used in 15 wt % composition with Ketjen Black, in cathode MPL of DMFCs has effectively decreased the mass transport
resistance, owing to the pore structure/particle size characteristics coupled with the disruptive nature of stacking KB and AC leading to a cracked, more open structure. However, when used in higher weight percentages such as 25, 50, 75 and 100 wt % compositions, this resulted in poor performance caused by the poor electrical conductivity of the material affecting the electrical contact between the catalyst layer and GDL. If the electrical conductivity of the activated carbon could be further improved, this would lead to fuel cells, being operated at higher load conditions, without the need for increased catalyst loading by improvement in performance up to 33 %.

The water management at the cathode is a relatively simple process in a DMFC as it only relates to the escape of water from the catalysis layer which was the subject of this study. There may be some benefit in using an AC/KB mixture at the anode but there would be a competition between the ingress of the methanol water mixture to the catalysis layer and providing a pathway for CO₂ escape and would therefore a significantly more complex issue.

In addition to the chemical benefits, the usage of biomass based materials as electrodes in fuel cell electrodes will significantly reduce the reliance on conventional, expensive carbon precursors. The choice of waste tea activated carbon was due to the accessibility of highly characterised material with known electro-chemical properties. It is highly likely that a systematic study of other activated carbons would show that some materials have better properties for use in fuel cells but this would require a systematic study of all available carbons.

Acknowledgements

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References


Figure Caption
Fig. 1 Characterization of synthesized activated carbon sample (a) Nitrogen adsorption-desorption isotherm (b) Pore size distribution [19].
Fig. 2 SEM images of electrodes (MPL) coated with (a) KB and different weight percentages of AC (b) 15 wt% AC (c) 25 wt% AC (d) 50 wt % AC (e) 75 wt % AC (f) 100 wt % AC.
Fig. 3 Particle size distribution analysis of KB and AC.
Fig. 4 (a&b) Current and power density profile for standard, 5 wt % AC, 10 wt % AC, 15 wt % AC (c&d) Current and power density profile for standard, 25 wt % AC, 50 wt % AC, 75 wt % AC, 100 wt % AC electrodes obtained at the following conditions: 70 °C, 1 M MeOH, 1 LPM of air (e) Illustration of different regions in a general current density plot (fuel cell polarization curve).
Fig. 5 Tafel plot for standard and 15 wt % AC electrodes obtained at the following conditions: 70 °C, 1 M MeOH, 1 LPM of air.
Fig. 6 Effect of temperature on power density for standard and 15 wt % AC electrode.
Fig. 7 (a) Representation of the information which can be extracted from the impedance plot; Comparison of impedance plot for standard and 15wt% activated carbon (b) Activation region (0.6 V) (c) Ohmic region (0.3 V) (d) Mass transport region (0.1 V) (e) Comparison of electrode reaction resistance values at different regions in a polarization curve.
Fig. 8 Durability measurements obtained at (a) low current density (100 mA cm⁻²) (b) high current density (325 mA cm⁻²) region in the following conditions: 70 °C, 1 M MeOH, 1 L min⁻¹ of air.
Fig. 9 Effect of AC wt % on through-plane and in-plane electrical conductivity and performance of MPLs.
### Table 1. Elemental composition (EDS) analysis of synthesized activated carbon sample

<table>
<thead>
<tr>
<th></th>
<th>C (%)</th>
<th>O (%)</th>
<th>N (%)</th>
<th>H (%)</th>
</tr>
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<tbody>
<tr>
<td>EDS</td>
<td>84.97</td>
<td>11.24</td>
<td>1.11</td>
<td>2.68</td>
</tr>
</tbody>
</table>

### Table 2. Pore characteristics and specific surface area of synthesized activated carbon (AC) [19] and Ketjen Black (KB)

<table>
<thead>
<tr>
<th></th>
<th>Specific surface area (m² g⁻¹)</th>
<th>Total pore volume a (cm³ g⁻¹)</th>
<th>Micropore volume b (cm³ g⁻¹)</th>
<th>Mesopore volume c (cm³ g⁻¹)</th>
<th>Microporosity (%)</th>
<th>Mesoporosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC:</td>
<td>1327</td>
<td>1.142</td>
<td>0.2778</td>
<td>0.8651</td>
<td>24.31</td>
<td>75.69</td>
</tr>
<tr>
<td>KB:</td>
<td>1364</td>
<td>2.334</td>
<td>0.1362</td>
<td>2.1988</td>
<td>5.84</td>
<td>94.16</td>
</tr>
</tbody>
</table>

a At P/P₀ = 0.99; b At 2 nm; c Total volume – micropore volume
Table 3. Electrode characteristics (porosity, contact angle and air permeability) of electrode (MPL) coated with KB and different weight percentages of AC

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Contact angle (± 2)</th>
<th>Porosity (%)</th>
<th>Hydrophobic porosity (%)</th>
<th>Hydrophilic porosity (%)</th>
<th>Gas permeability (Barrer) (± 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt% AC</td>
<td>106</td>
<td>70 ± 2</td>
<td>63 ± 3</td>
<td>37 ± 3</td>
<td>60</td>
</tr>
<tr>
<td>5 wt% AC</td>
<td>108</td>
<td>68 ± 1</td>
<td>65 ± 2</td>
<td>35 ± 1</td>
<td>58</td>
</tr>
<tr>
<td>10 wt% AC</td>
<td>110</td>
<td>67 ± 3</td>
<td>68 ± 1</td>
<td>32 ± 2</td>
<td>55</td>
</tr>
<tr>
<td>15 wt% AC</td>
<td>113</td>
<td>65 ± 1</td>
<td>71 ± 1</td>
<td>29 ± 1</td>
<td>52</td>
</tr>
<tr>
<td>20 wt% AC</td>
<td>115</td>
<td>63 ± 1</td>
<td>73 ± 4</td>
<td>27 ± 4</td>
<td>50</td>
</tr>
<tr>
<td>25 wt% AC</td>
<td>118</td>
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<td>75 ± 1</td>
<td>25 ± 1</td>
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</tr>
<tr>
<td>50 wt% AC</td>
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<td>55 ± 2</td>
<td>81 ± 3</td>
<td>19 ± 3</td>
<td>46</td>
</tr>
<tr>
<td>75 wt% AC</td>
<td>134</td>
<td>51 ± 1</td>
<td>87 ± 1</td>
<td>13 ± 1</td>
<td>44</td>
</tr>
<tr>
<td>100 wt% AC</td>
<td>143</td>
<td>49 ± 4</td>
<td>91 ± 2</td>
<td>9 ± 2</td>
<td>42</td>
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</tbody>
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